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⑫ **EUROPEAN PATENT APPLICATION**

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(71) Applicant: **AUSIMONT S.p.A.**
Foro Buonaparte, 31
I-20121 Milano(IT)

(72) Inventor: **Giampaolo, Solinas**
Via Corridoni 36
I-21053 Castellanza (Varese)(IT)
Inventor: **Giampiero, Basile**
Via San G. Bosco, 37
I-15100 Alessandria(IT)

(74) Representative: **Simeoni, Lucio, Dr.**
Sama Patents,
Via Masera, 10 (P.zza Lima)
I-20129 Milano (IT)

(54) Process for separating hydrogen fluoride from its mixtures with chlorofluorohydrocarbons 123 and/or 124.

(57) The invention relates to a process for separating HF contained in liquid mixtures comprising HCFC 123 and/or 124. The mixtures, enriched in C_2Cl_4 up to a content of such compound of 20-75% by weight, is subjected to a treatment for separating liquid phases, thereby obtaining an acid phase very rich in Hf and an organic phase impoverished in HF, which is subjected to a flash, so obtaining a liquid phase containing 123, 124 and C_2Cl_4, having a very low HF content, and a gas phase enriched in HF. As an alternative to flash, a separation in a distillation column can be carried out.

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The present invention relates to a process for separation of hydrofluoric acid from is mixtures with 1,1,1-trifluoro-2,2-dichloroethane (HCFC 123) and/or 1,1,1,2-tetrafluoro-2-chloroethane (HCFC 124) and other halocarbon compounds, if any.

Various methods of separating and recovery HF from fluorocarbon composition are described in the art.

According to U.S. patent No. 3,406,099, the separation of CF_3COCF_3, HF and $CFCl_2$ $CClF_2$ from their mixtures is carried out via azeotropic distillation.

U.S. patent No. 3,947,558 describes a process for separating HF from the fluorination products of chlorocarbons having 1-3 carbon atoms, which comprises the initial step of separating HCl, if any, then cooling the mixture in order to obtain two liquid phases, one rich in HF and the other poor in HF, and treating the latter with a glycol having 2-8 carbon atoms, so obtaining a glycolic phase rich in HF, which is then recovered by distillation.

According to U.S. patent No. 4,209,470, HF is separated from its liquid mixtures with 1-chloro-1,1-difluoroethane by addition of an auxiliary solvent selected from 1,1-dichloro-1-fluoroethane, vinylidene chloride and 1,1,1-trichloroethane with separation of a liquid phase impoverished in HF, from which HF is then separated by distillation.

Lastly, according to U.S. patent No. 4,944,846, the separation of HF from its mixtures with HCFC 123 and/or 124 is obtained by regulating the HF/HCFC 123 molar ratio in such mixture to values not exceeding 1.3, and then by subjecting said mixture to azeotropic distillation, thereby obtaining a head portion containing substantially all the HF and a part of HCFC 123 in the form of a HF/HCFC 123 azeotrope and, maybe, a HF/HCFC 124 azeotrope and a tail portion substantially free from HF, containing HCFC 123.

The Applicant has now found a process for separating HF from its mixtures comprising HCFC 123 and/or HCFC 124 which does not require azeotropic distillations.

In fact, the Applicant has surprisingly found that it is possible to obtain a separation of the HF contained, even in small concentrations, in liquid mixtures comprising HCFC 123 and/or HCFC 124, if a C_2Cl_4 amount ranging from 20 to 75% by weight calculated on the total of the mixtures, is added to such mixtures and if they are subjected to a treatment for separating two liquid phases, under particular conditions, so obtaining an organic phase poor in HF, which is subjected to a partial vaporization by flash according to particular modalities.

From the flash treatment, a head portion (vapour phase) enriched in HF, comprising HCFC 124 and HCFC 123 and small amounts of C_2Cl_4, and a tail portion (liquid phase), substantially free from HF and containing HCFC 123, HCFC 124 and C_2Cl_4 are obtained.

Thus, it is an object of the present invention to provide a new process for separating HF from its mixtures containing HCFC 123 and/or HCFC 124.

Another object is to provide a process, simplified with respect to those of the prior art, which allows in particular, when so desired, the use of distillation columns to be avoided.

These and still other objects are achieved by the process of the present invention for separating HF contained in liquid mixtures comprising hydrochlorofluorocarbons 123 and/or 124.

This process is characterized in that:

1) to such mixtures, tetrachloroethylene is added in such amounts that the proportion by weight of tetrachloroethylene ranges from 20 to 75% by weight in the resulting mixtures, such operation not being required if the mixtures to be treated comprising HF, 123 and/or 124 already exhibit a tetrachloroethylene content in the above indicated range;

2) maintaining the mixtures coming from the first step at a temperature selected in the range of from -40°C to +50°C and a pressure equal to or higher than the total vapour tension of the mixtures at the above said temperature, obtaining two liquid phases, which are separated, the lighter one having a very high HF content and the denser one being an organic phase impoverished in HF;

3) the organic phase is subjected to a partial vaporization treatment by means of flash, operating so as to obtain a vaporization of 15-60% by weight of the inflowing organic phase, under a pressure ranging from 0.1 to 2 Mpa abs.;

4) after having substantially reached the equilibrium between the gas phase and the liquid phase, the liquid phase, substantially free from HF and containing HCFC 123, HCFC 124 and tetrachloroethylene, is separated from the gas phase enriched in HF and containing HCFC 123, HCFC 124 and tetrachloroethylene.

According to an alternative to such process, after having carried our steps 1) and 2) described hereinbefore, the organic phase is subjected to separation in a distillation column, according to the art.

The partial vaporization by means of flash - usually referred to as "flash" by the technicians - is, as is known, an operation in which a liquid mixture is partially vaporized in an apparatus having appropriate dimensions, in which the two phases (gaseous and liquid) are maintained in contact until the equilibrium between them is substantially reached, then they are separated and removed from the apparatus.

The step in which the two liquid phases are formed and separated, according to the present invention, can be effected either continuously of discontinuously.

The separation is carried out by means of known techniques such as gravity deposition, centrifugation and flow through porous membranes.

Is said step for the formation and separation of the two liquid phases, it is preferably operated at temperatures ranging from 0 to 30 °C and at pressures preferably ranging from 0.1 to 1 Mpa abs. The liquid acid phase can be conveniently recycled to the HCFC synthesis reactor.

In the flash operation, which can be conduced continuously of discontinuously, preferably a pressure ranging from 0.5 to 1.0 Mpa abs is operated. Preferably, such operation is conducted so as to vaporize from 20 to 50% by weight of the inflowing organic phase.

The vapour phase is preferably recycled at a point in the plant between the HCFC synthesis and the separation of the liquid phases.

The liquid phase obtained at the end of flash has such a low residual HF content that in several cases it is not necessary to remove the residual HF because, for example, it will be at any rate eliminated during the purification operations of the HCFC to be obtained.

However, if so desired, the residual HF of the liquid phase can be removed by means of conventional techniques: for example, it is possible to vaporize the liquid phase and to treat it with an alkaline aqueous solution, whereafter the organic components can be separated from one another by distillation.

While the HF-containing mixture, which is treated according to the present invention, can come from various sources, an advantageous embodiment of the present invention resides in treating the mixture flowing from the preparation of HCFC 123 and/or 124 by reaction of tetrachloroethylene with HF, for example conforming to the process of U.S. patent No. 4,967,023.

The mixture coming from such reaction usually comprises HF, HCFC 123 and 124, tetrachloroethylene, HCl and minor amounts of halogenated compounds such as 1,2,2-trichloro-1,1-difluoroethane (HCFC 122) and perfluoroethane (HFC 125).

In this case, the mixture to be treated is preferably deprived in advance of HCl and HFC 125 contained in it by means of conventional techniques, for example by distillation or rectification.

Of course, if the mixtures obtained from such reaction contain amounts of tetrachloroethylene lower than 20% by weight, it will be necessary to secure that the content of such composition in the mixture is in the required range of from 20 to 75% by weight, as indicated hereinbefore, by effecting suitable additions of said compound to the mixture to be treated.

The following examples are given merely for the purpose of illustration and are not intended to limit the scope of the invention. In said examples, the pressures are indicated in absolute values.

All the compositions of the mixtures have been determined by gas chromatography for the organic components and by acidimetric titration with regard to HF. Each analysis has been carried out 4 times, and the compositions reported in the Tables indicate the average values determined in such analyses.

Also in the flash operation, the vaporization degree of the inflowing organic phase is indicated as average value.

EXAMPLE 1

A gaseous phase coming from a synthesis process of 123 and 124 by hydrofluorination reaction of C_2Cl_4 was condensed at 25 °C. C_2Cl_4 was added to the liquid phase until composition A reported in Table 1 was obtained. The liquid phase enriched in C_2Cl_4 was treated in a liquid phase separator of about 2 litre volume, where a pressure of 0.3 MPa was dominant.

From the separator, an upper phase essentially consisting of HF and a lower organic phase of composition B (see Table 1) were drawn. From the organic phase having composition B, a sample of 141.2 g was taken, which was subjected to flash in a pressure vessel of 1.060 litre volume.

The pressure in the vessel was 0.5 MPa and the temperature was 60.3 °C. Once the equilibrium between vapour phase and liquid phase had been reached, which was apparent from the constant temperature and pressure (the operation was conducted, for operative convenience, over 14 hours), the vapour phase percentage was of 14% by weight. Then, the two phases were separated.

The gaseous phase had composition C reported in Table 1, while the liquid phase had composition D, also reported in Table 2.

TABLE 1

Components	Composition A: fed to the liquid phase formation and separation step (% by weight)	Composition B: liquid organic phase obtained after liquid phase separation (% by weight)	Composition C: vapor phase obtained by means of flash (% by weight)	Composition D: liquid phase obtained by means of flash (% by weight)
C_2Cl_4	29.4	29.8	1.2	36.4
HCFC 123	34.2	34.6	26.5	37.9
HCFC 124	34.4	34.8	71.1	25.6
HF	2.0	0.8	1.2	0.09

EXAMPLE 2

Starting from a different mixture enriched in C_2Cl_4, the general procedure of example 1 was followed, except that:

- the amount of organic phase fed to flash was of 139.5 g;
- in the flash vessel, the temperature was of 79.3 °C.

The vaporization degree was 27% by weight.

The compositions of the various phases are reported in Table 2.

TABLE 2

Components	Composition A: fed to the liquid pahse formation and separation step (% by weight)	Composition B: liquid organic phase obtained after liquid phase separation (% by weight)	Composition C: vapor phase obtained by means of flash (% by weight)	Composition D: liquid phase obtained by means of flash (% by weight)
C_2Cl_4	49.0	49.9	5.57	63.0
HCFC 123	29.5	29.9	28.0	24.05
HCFC 124	19.5	19.9	55.3	12.9
HF	2.0	0.3	0.95	0.045

EXAMPLE 3

Starting from another mixture enriched in C_2Cl_4, the general procedure of example 1 was followed, except that:

- the amount of organic phase fed to flash was of 152.1 g;
- in the flash vessel, the temperature was 108.5 °C.

The vaporization degree was equal to 27% by weight.

The compositions of the various phases are reported in Table 3.

TABLE 3

Components	Composition A: fed to the liquid phase formation and separation step (% by weight)	Composition B: liquid organic phase obtained after liquid phase separation (% by weight)	Composition C: vapor phase obtained by means of flash (% by weight)	Composition D: liquid phase obtained by means of flash (% by weight)
C_2Cl_4	68.5	70.0	18.7	84.2
HCFC 123	19.6	19.9	34.8	13.0
HCFC 124	9.8	10.0	45.6	2.8
HF	2.1	0.12	0.90	0.02

EXAMPLE 4

This example illustrates a flash operation.

A liquid mixture (614 g) of composition B was subjected to a flash operation according to the general modalities of example 1, with the exception that in the flash vessel, which had a volume of 610 ml, the pressure was of 0.66 MPa and the temperature of 78.6 °C.

The compositions of vapour phase C and liquid phase D obtained by means of flash are reported in Table 4.

TABLE 4

Components	Composition B: liquid organic phase subjected to flash (% by weight)	Composition C: vapor phase obtained by means of flash (% by weight)	Composition D: liquid phase obtained by means of flash (% by weight)
C_2Cl_4	39.93	1.713	40.23
HCFC 123	39.93	33.287	39.98
HCFC 124	20.05	64.25	19.70
HF	0.094	0.75	0.090

Claims

1. A process for separating HF contained in liquid mixtures comprising hydrochlorocarbons 123 and/or 124, characterized in that:
   1.) tetrachloroethylene is added to such mixtures in such amount that the proportion by weight of tetrachloroethylene ranges from 20 to 75% by weight in the resulting mixtures, such operation not being necessary if the mixtures comprising HF, hydrochlorofluorocarbon 123 and/or hydrochlorofluorocarbon 124, to be treated already exhibit a tetrachloroethylene content in the above-indicated range;
   2.) maintaining the mixtures coming from the first step at a temperature selected from values ranging from -40°C to +50°C and at a pressure equal to or higher than the total vapour tension of the mixtures themselves at the above said temperature, two liquid phases are caused to form, which are separated, the lighter one having a very high HF content and the denser one being an organic phase impoverished in HF;
   3.) the organic phase is subjected to a partial vaporization operation by means of flash by operating in such manner as to obtain a vaporisation of 15-60% by weight of the inflowing organic phase, under a pressure ranging from 0.1 to 2 MPa abs;
   4.) after having substantially reached the equilibrium between gaseous phase and liquid phase, the liquid phase, substantially free from HF and containing HCFC 123, HCFC 124 and tetrachloroethylene, is separated from the gaseous phase enriched in HF and containing HCFC 123, HCFC 124 and tetrachloroethylene.

2. A process for separating HF in liquid mixtures comprising hydrochlorofluorocarbons 123 and/or 124, characterized in that, after having carried out steps 1.) and 2.) described in claim 1, the organic phase is subjected to separation in a distillation column, according to the conventional technique.

3. The process according to claim 1 or 2, characterized in that in the operation for forming and separating the two liquid phases, the temperature ranges from 0 to 30°C.

4. The process according to one more of claims 1 to 3, characterized in that in the operation for forming and separating the two liquid phases, the pressure ranges from 0.1 to 1 MPa abs.

5. The process according to one or more of claims 1, 3 and 4 characterized in that in the flash operation, the pressure ranges from 0.5 to 1.0 MPa abs.

6. The process according to one or more of claims 1, 3, 4 and 5, characterized in that the partial vaporization of the liquid organic phase by means of flash is conducted in such manner as to obtain a vaporization of 20-50% by weight.

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EUROPEAN SEARCH REPORT

Application Number
EP 93 11 8728

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	EP-A-0 353 970 (E.I. DU PONT DE NEMOURS AND COMPANY) 7 February 1990 * page 3, line 1 - line 19 * * page 3, line 44 - page 4, line 33 * * claims 1,2 *	2	C01B7/19 C07C17/38
Y	IDEM ---	1-5	
D,Y	EP-A-0 003 147 (SOLVAY & CIE) 25 July 1979 * page 2, line 17 - page 3, line 11 * * page 4, line 9 - line 14 * * page 4, line 23 - page 5, line 6 * * page 5, line 24 - page 6, line 24 * * page 10, line 33 - page 11, line 10 * ---	1-5	
A	GB-A-718 682 (E.I.DU PONT DE NEMOURS AND COMPANY) 17 November 1954 * page 1, line 16 - line 22 * * page 1, line 80 - page 2, line 50 * * examples * -----	1,2,4,5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C01B C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	8 March 1994	Van der Poel, W

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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